

GAU 1621

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Applicants: Buchwald, S.L. et al.

Examiner: Barts, S.

AUG 30 2001

Application Serial No.: 09/239,024

Art Unit: 1621

TECH CENTER 1600/2900

Filed: January 27, 1999

Atty. Docket No.: MTV-009.02

Title: *Arylation and Vinylation of Activated Carbons*Assistant Commissioner for Patents  
Washington, DC 20231

## Certificate of Mailing

I hereby certify that this "Declaration Under 37 CFR § 1.131" is being deposited with the U. S. Postal Service as First Class Mail with sufficient postage on the date set forth below in an envelope addressed to:

Assistant Commissioner for Patents, Washington, D.C. 20231.

8/24/01

By: Dana Gordon

Date of Signature and Mail Deposit

Dana Gordon

## Declaration Under 37 CFR § 1.131

Dear Examiner Barts:

As an inventor named on the above-identified application, I hereby declare that the subject matter of rejected claims 1-35 was invented in the United States prior to the effective date, October 16, 1997, of United States Patent 6,057,456.

In support of this Declaration, I attach hereto copies of pages, with their entry dates redacted, from laboratory notebooks maintained by me or one or more of my joint inventors, establishing a reduction to practice of the subject matter of the rejected claims prior to the effective date, October 16, 1997, of United States Patent 6,057,456. Notwithstanding the fact that the entry dates on these pages have been redacted, I hereby declare that these documents establish that a reduction to practice of the subject matter of the rejected claims took place in the United States prior to the effective date, October 16, 1997, of United States Patent 6,057,456.

I hereby declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Stephen L. Buchwald: Stephen L. BuchwaldDate: 8/23/01

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Control 267 c1ccccc1 + NaOH  $\xrightarrow{\text{Toluene, } 70^\circ\text{C}}$  No prod

269, CN(C1=CC=CC=C1)C2=CC=CC=C2 + CC(O)C + Kult. DMF, 70°C

275 (see above - at 70<sup>th</sup>)

277 BrC1=CC=CC=C1 + C1=CC=CC=C1  $\xrightarrow{\text{Pd(PPh}_3)_4, \text{PPh}_3, \text{Toluene, 70}^\circ\text{C}}$  No prod

[illegible]

284 BrC1CCC(CC1)C2=CC=CC=C2 + C1=CC=CC=C1 + NMA Pd(PPh3)4, Tol-Soln, 70°C, THF  $\rightarrow$  O=C1CCC(CC1)C2=CC=CC=C2 59 (61)

288  $\text{Br}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{Br} + \text{C}_6\text{H}_5\text{MgBr} + \text{Nal}$  Phenylmagnesium Bromide, Toluene,  $70^\circ\text{C}$   $\rightarrow$  Prod

284 BrC1=CC=CC=C1 + O=C1C=CC(=O)O1 + NaOAc  $\xrightarrow[\text{in } \text{CH}_2\text{Cl}_2]{\text{PBr}_3, \text{THF}, 50^\circ\text{C}}$  BrC1=CC=CC=C1C(=O)O1C=CC(=O)O1 + BrC1=CC=CC=C1C(=O)O1C=CC(=O)O1

234  $\text{Br}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{Br}$  +  $\text{C}_6\text{H}_5\text{NH}_2$  Positron, Tol. Gmp,  $\text{CuNO}_2$ , Tollen,  $\text{Na}^+$  No p'nd

240  $\text{Br}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{Br}$  +  $\text{C}_6\text{H}_5\text{NH}_2$  " " " " No p'nd

241. BrC1CCC(CC1)C(=O)O + CC1=CC=CC=C1 + Na2CO3  $\xrightarrow[\text{THF, } \Delta]{\text{SOCl}_2}$  CC1=CC=CC=C1C(=O)OC1CCC(Br)CC1

202 BrC1=CC=CC=C1 + c1ccccc1 + NaOMe  $\xrightarrow[\text{Alkyl, DPF, TOL, Zn}^{0}]{\text{Pd(PPh}_3)_3, \text{DPPH, TOL, Zn}^{0}}$  BrC1=CC=CC=C1C2=CC=CC=C2 38% 61

24.  $\text{C}_6\text{H}_5\text{COOH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{Na}^+$   
 25.  $\text{C}_6\text{H}_5\text{COOH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{Na}^+$

244 b. c1ccccc1 + c1ccccc1 + NaOH → Phenylacetylene

245 c. c1ccccc1 + c1ccccc1 + NaOH → Toluene

245 e. 235 + C + Mewat - 10/18/21  
246 - OPP E - no p.w

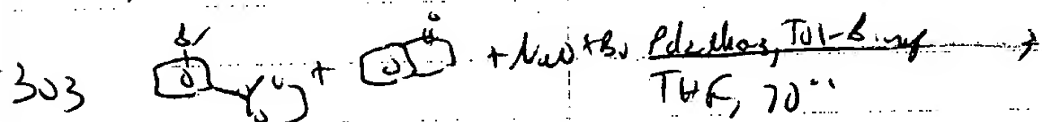
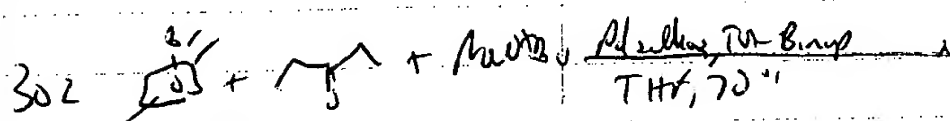
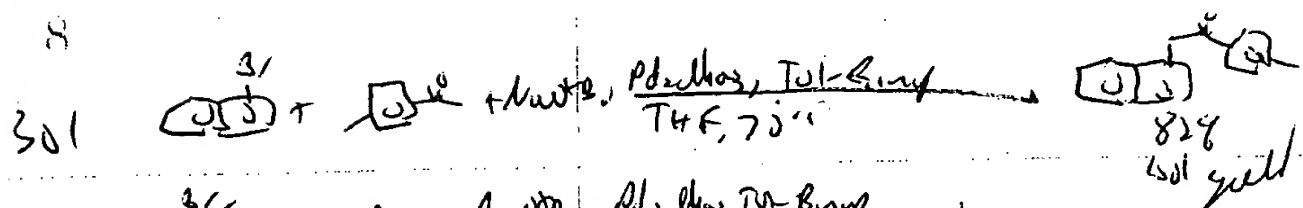
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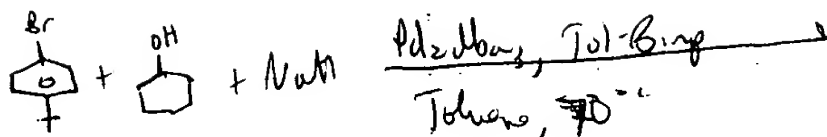
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09/239,024



Compound	MW	equiv	mmole	amount	volume
t-Butyl bromide	213.12	1.0	0.5	55 ml	
cyclopentanol	86.13	5.0	2.5	363 ul	
NaH (60%)	23.44	6.0	3.0	120 mg	
Pd2Mg	415.7	0.015	0.0075	6.4 mg	
Tol-Bing	678.74	0.036	0.008	12.2 mg	
Toluene				4 ml	

An oven dried Schlenk flask equipped with a stir bar was charged with NaH, evacuated and back filled with argon. To this was added 3 ml of Toluene and cyclopentanol. The mixture was heated to 70°C for 10 min, at which time t-Butyl bromide, Pd2Mg, Tol-Bing and 1 ml of Toluene were added. The resulting mixture was heated to 70°C while under argon.

1/26/96 - after 15 hrs, took aliquot

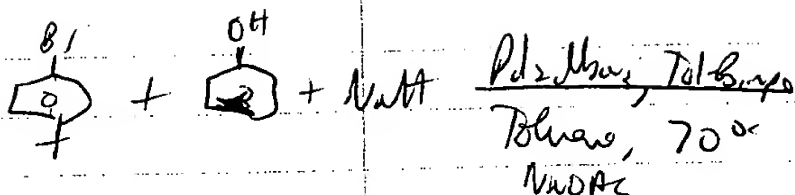
MP 61-II-282-1

87%

44%

2.7% p-ol, 2.7%

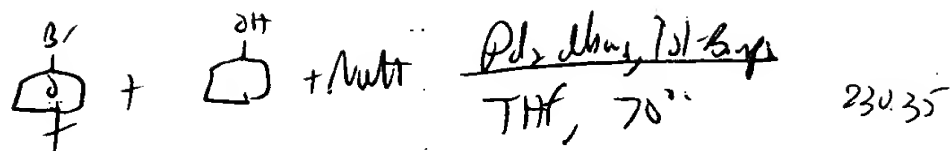
MP 60MS-II-282-1



Compound	MW	equiv	mmole	amount
+ Butyl benzoate	213.12	1.0	0.5	55 ml
Cyclohexanone	98.13	1.2	0.6	87 ml
NaOH (60%)	23.41	2.0	1.0	40 mg
Pd2Mn	915.7	0.015	0.0075	6.4 mg
NaOAc	82.03	1.0	0.5	41.0 mg
Tol-Benz	676.74	0.036	0.018	12.2 mg
Toluene				3 ml

An oven dried Schlenk flask containing a stir bar was charged w/ NaOH, evacuated and back filled w/ argon. To this was added + butyl benzoate, Pd2Mn, NaOAc, Tol-Benz and 1 ml of toluene. Cyclohexanone and 2 ml of toluene. The mixture was heated for 10 min at 70°C at which time + butyl benzoate, Pd2Mn, Tol-Benz, NaOAc and 1 ml of toluene was added. The mixture was heated to 70°C while under argon.

11/26/96 - after 15 hours, took aliquot 
  
 MP 66-72-283-1 65.6 
  
 32.5 
  
 3.9



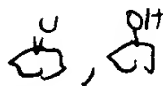
Compound	MW	equiv	mmole	amount
t-butyl bromide	213.12	1.0	0.5	55ml
cyclohexanol	98.15	1.2	0.6	87ml
NH <sub>4</sub> NO <sub>3</sub> (60%)	23.47	2.0	1.0	40mg
Pd <sub>2</sub> dcl <sub>2</sub>	415.1	0.017	0.0075	6.9mg
tol-Bing	678.74	0.036	0.018	12.2mg
Toluene				3ml

An oven dried Schlenk flask containing a stir bar was charged with N#N, mounted and back filled with argon. To this was added 2ml of THF and cyclohexanol. The mixture was heated to 70° for 10 min, at which time t-butyl bromide, Pd<sub>2</sub>dcl<sub>2</sub>, tol-Bing and 1ml of THF were added. The mixture was heated to 70° while under argon.

11/26/71 - after ~ 20 hrs, toluene added

MP 66-67-284-1

67%



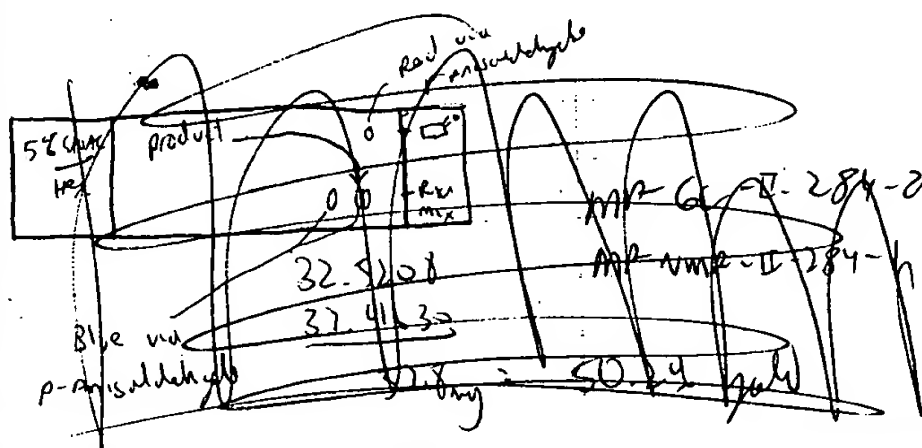
27%

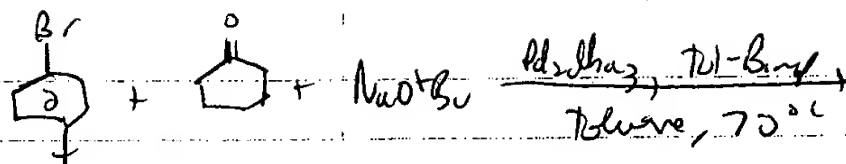


5%




5%



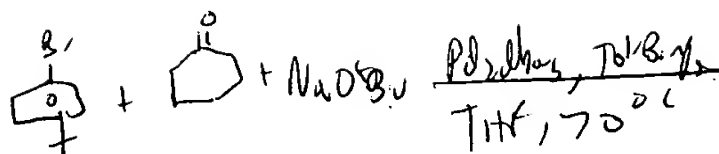


Compound	MW	equiv	mole	amount	note
t-Butyl Bromide	213.12	1.0	0.5	55 ml	
Cyclohexanone	98.15	1.2	0.6	62 ml	
NaOEt	16.7	1.3	0.65	65 mg	
Pd <sub>2</sub> daz	415.7	0.005	0.0075	6.4 mg	
Tol-Bing	678.74	0.036	0.008	12.2 mg	
Toluene				3 ml	

An oven dried Schlenk flask containing a stir bar was charged w/ NaOEt (from the box), Pd<sub>2</sub>daz, Tol-Bing and 2 ml of Toluene (all under Argon). To this was added t-Butyl Bromide, cyclohexanone and 1 ml of Toluene. The resulting mixture was heated to 70°C while under argon.

After 6 hours, took aliquot MP GC-D-285-1  
15% , 65% prod - others

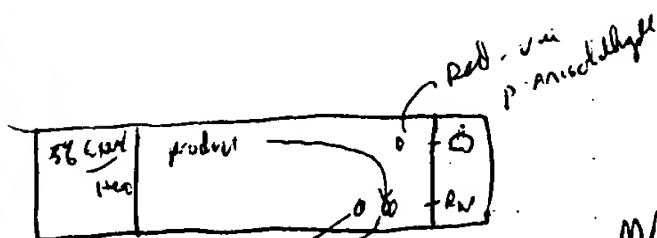




Compound	MW	equiv	mmole	amount	notes
<i>t</i> -butyl bromide	213.12	1.0	0.5 (0.31)	55ml	should be 87ml
cyclohexanone	98.15	1.2	0.6	62ml	
NaO <sup>t</sup> Bu	96.1	1.3	0.65	65mg	
Pd <sub>2</sub> dhs	915.1	0.015	0.0071	6.4mg	
Tol-B-mp	678.74	0.031	0.018	11.1mg	
+ THF				3ml	

An oven dried Schlenk flask containing a stir bar was charged w/ NaO<sup>t</sup>Bu (Box), Pd<sub>2</sub>dhs and Tol-B-mp (under argon). To this was added THF, *t*-butyl bromide and cyclohexanone. The resulting mixture was heated to 70°C while under argon.

After 6 hrs, took aliquot - MP 61-71-281-1  
 23%  $\text{C}_{12}\text{H}_{17}\text{Br}$ , 73% prod, NO SM, NO  $\text{C}_{12}\text{H}_{17}\text{Br}$

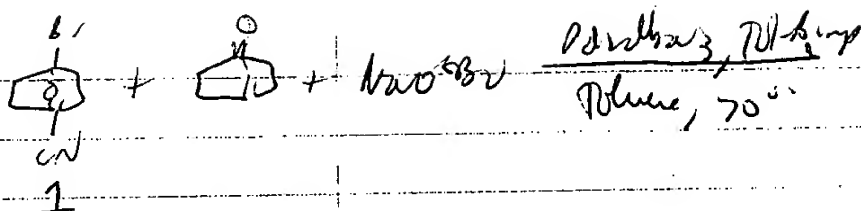


stop  
 via - P-arsenide

32.5206  
 37.4632

57.8 mg = 79.8% yield

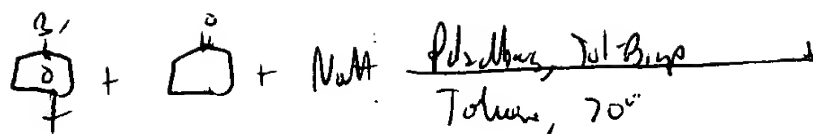
MP 65-71-286-2  
 MP-NMR-II-286-2



Compound	MW	equiv	mmole	amount	source
4-bromobenzonitrile	182.03	1.0	0.5	91mg	
cyclohexanone	98.15	1.2	0.6	62ml	0.9g
NaOEt (91%)	96.7	1.3	0.65	65mg	
Tol-B	678.74	0.036	0.008	12mg	
Toluene				3ml	
Pd(PPh3)4	415.7	0.045	0.0075	6.4mg	


An oven dried Schlenk flask containing a stir bar was charged w/ NaOEt (Box), Pd(PPh3)4, Tol-B and, 1, then 2 ml of Toluene & all under argon. To this was added cyclohexanone and 1ml of Toluene. The mixture was heated to 70°C while under argon.

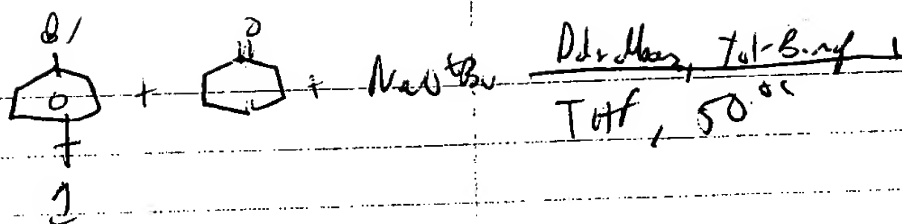
after 4 hours took aliquot MP GC-II-287-1



Compound	MW	equiv	mmole	amount	conv
t-Butyl bromide	213.12	1.0	0.5	55 ml	
Cyclohexane	98.15	1.2	0.6	62 ml	
NaH (60%)	23.99	1.3	0.65	26 mg	
Pd, Alkyl	915.7	0.015	0.0075	6.9 mg	
Tol-Bmp	678.74	0.036	0.018	12 mg	
Toluene				3 ml	

An oven dried Schlenk flask containing a tin bar was charged w/ NaH, evacuated and back filled w/ argon. This was added Pd, Alkyl, Tol Bmp, t-Butyl bromide, cyclohexane and 3 ml Toluene. The mixture was heated to 70° while under argon.

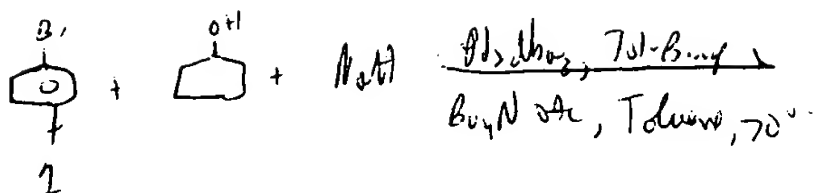
After 6 hours, took aliquot  
 MP 61-II-288-1 48%   
 46% SM



Compound	MW	equiv	mmole	amount	volume
1	213.12	1.0	0.5	55ml	
cyclohexene	98.15	1.2	0.6	62ml	
NeotBu	46.7	1.3	0.65	65mg	
PdCl <sub>2</sub>	95.7	0.015	0.015	6.4mg	
Tol-Bing	678.74	0.036	0.018	12.2mg	
THF				3ml	

An oven dried Schlenk flask containing a stir bar was charged NeotBu, PdCl<sub>2</sub>, Tol-Bing evacuated and back filled w/ argon. 2 - this was added 1, cyclohexene and 3 ml of THF. The mixture was heated to 50°C while under argon.

After 3 hours, took aliquot MP-65-II-289-1  
218 8.49 gm, 67.39 prod



start 1:00p

Compound	MW	equiv	mmol	amount	source
1	213.11	1.0	0.5	55 ml	
cyclohexanol	98.12	1.2	0.6	62.4 ml	
NaOH (60%)	23.14	2.0	1.0	40.0 g	
Bu <sub>4</sub> N <sup>+</sup> Ac <sup>-</sup> (95%)	301.5	1.0	0.5	150.8 g	
Ph <sub>2</sub> O <sub>2</sub>	115.7	0.005	0.005	6.4 mg	
Tol-B	678.74	0.005	0.005	12.2 mg	
Toluene				3 ml	

An oven and Schlenk flask containing a stir bar was charged w/ NaOH, Bu<sub>4</sub>N<sup>+</sup>Ac<sup>-</sup> (in the bar), Ph<sub>2</sub>O<sub>2</sub>, Tol-B wags and was evacuated and back filled w/ argon. To this was added 1, cyclohexanol and 3 ml of Toluene. The mixture was heated to 70°C while under argon.

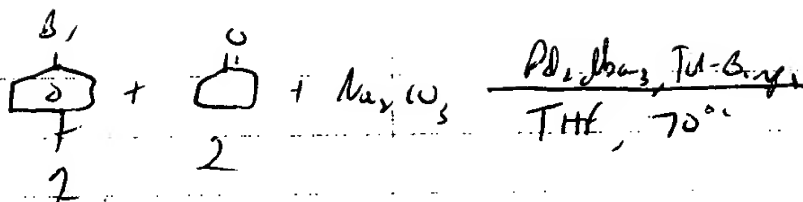
After 3 hours, Took aliquot. MP 61-II-240-1

58% , 20% , 21% RT = 2.41

11/30/91

After 22 hrs - Took aliquot MP 61-II-240-1

35% , 21% , 37% RT = 2.41



Sht 1:01

Compound	mm	equiv	mmol	amount
1	213.12	1.0	0.5	55ul
<del>Cyclohexanone</del> 2	18.15	1.2	0.6	62ul
Na <sub>2</sub> CO <sub>3</sub>	105.81	1.3	0.65	68.8mg
Pd <sub>2</sub> dba <sub>3</sub>	415.7	0.005	0.0015	6.9mg
Tol-B. mg	678.71	0.02	0.018	12.2mg
THF			3ml	

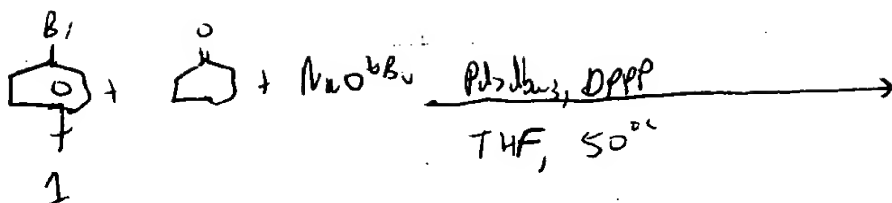
An oven dried Schlenk flask equipped w/ a stir bar was charged w/ Na<sub>2</sub>CO<sub>3</sub>, Pd<sub>2</sub>dba<sub>3</sub>, and Tol-B. The Schlenk flask was evacuated and back filled w/ argon. To this was added 1, 2 and 3 ml of THF. The mixture was held at 70°C while under argon.

after 3 hours, took aliquot - MP C1-E-291-1

449 48% SM no prod.

11/30/41 - after 22 hours, took aliquot  
MP C1-E-291-2 456 48% SM no prod.

Start 1:45p

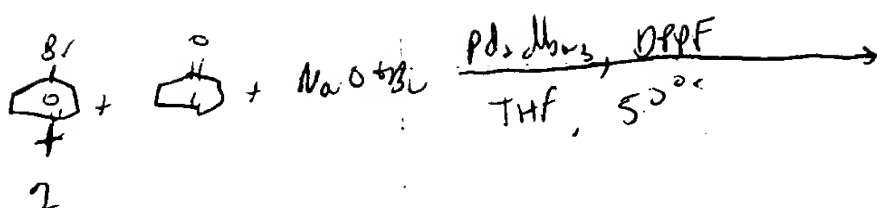


Compound	MW	equiv	mmole	amount	route
1 (172)	213.12	1.0	0.5	90ul	1.224
Cyclohexanone	98.15	1.2	0.6	62ul	
NaO <sup>t</sup> Bu (478)	46.7	1.3	0.65	65mg	
Pd <sub>2</sub> dvas	415.7	0.015	0.015	6.4mg	
DPPP	412.46	0.036	0.018	7.42mg	
THF				3ml	

An oven dried Schlenk tube was charged w NaO<sup>t</sup>Bu, Pd<sub>2</sub>dvas, DPPP, mounted and both filled w argon. To this were added 1, cyclohexanone and THF. The mixture was heated to 50°C while under argon.

After 3 hrs, Test aliquot - MP 61-62-1  
 35% ~~SM~~, 65% SM.

12/1/11 - after 24 hrs, Test aliquot MP 61-62-1  
 15% , 8% , 63% SM, 2% prod.



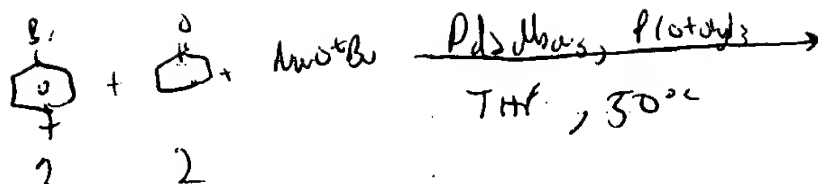
Compound	MW	equiv	mmole	amount	volume
2 (172)	213.12	1.0	0.5	90 $\mu$ l	
Cyclohexanone	98.15	1.2	0.6	62 $\mu$ l	
NaO <sup>+</sup> Bu (172)	16.7	1.3	0.65	65 mm	
Pd <sub>2</sub> Mn <sub>3</sub>	915.7	0.015	0.0075	6.9 mg	
DPPF	554.34	0.030	0.018	10 mg	
THF				3 ml	

An oven dried Schlenk tube was charged w/ NaO<sup>+</sup>Bu, Pd<sub>2</sub>Mn<sub>3</sub>, DPPF, evacuated and back filled w/ argon. 2. This was added 4, cyclohexanone, THF and the mixture was heated to 50°C under argon.

After 3 hours, Tost aliquot MP-61-II-293-1  
 23% 3.51 46.68 SM, 26% prod.

12/1/48 - After 24 hours, Tost aliquot MP-61-II-293-2  
 15.7% 19.4% 18% SM, 37.7% prod.







Start 1:00p

Compound	MW	equiv	mmole	amount	source
1 (97%)	213.12	1.00	0.5	90ul	
Cylohexane	98.15	1.2	0.6	62ml	
NaOEt (97%)	96.1	1.3	0.65	65ml	
Pd2dba3	115.1	0.015	0.0075	6.9mg	
P(tolyl)3	304.37	0.07	0.035	10.7mg	
THF	30			6ml	

An oven dried Schlenk flask containing a stir bar was charged w NaOEt, Pd2dba3, P(tolyl)3, and was evacuated and back filled w argon. 2-This was added 2 and 2 and THF. The mixture was heated to 50°C while under argon.

After 3 hr, took aliquot - MA 61-4-244-1

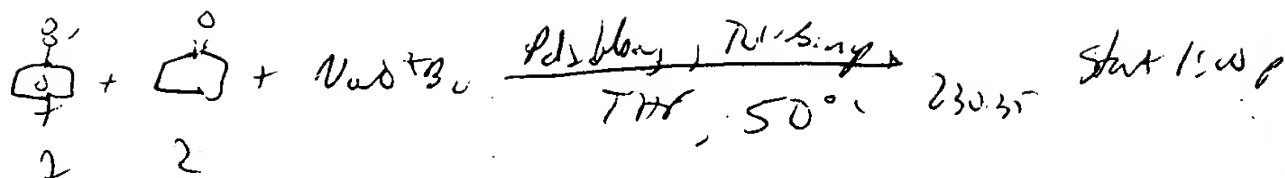
6% , 32% , 29% SM, no prod

12/1/96 - After 24 hours, took aliquot - MA 61-4-244-7

5% , 39% , 28% SM, 2% prod.

09/239,024

295



Compound	MW	equiv	mmole	amount
1 (47%)	213.12	1.0	0.5	10 ml
Cyclohexanone	98.15	1.2	0.6	62 ml
NaO <sup>t</sup> Bu (47%)	96.1	1.3	0.65	65 ml
Pd <sub>2</sub> dcl <sub>2</sub>	455.1	0.015	0.0075	6.9 mg
P <sup>t</sup> -Bing	678.74	0.25	0.0125	12.2 mg
THF				5 ml

An over Schlenk flask was charged w/ NaO<sup>t</sup>Bu, Pd<sub>2</sub>dcl<sub>2</sub>, P<sup>t</sup>-Bing and was evacuated and back filled w/ argon. 2  
 This was added 1 and 2, THF and the mixture heated  
 to 50°C while under argon

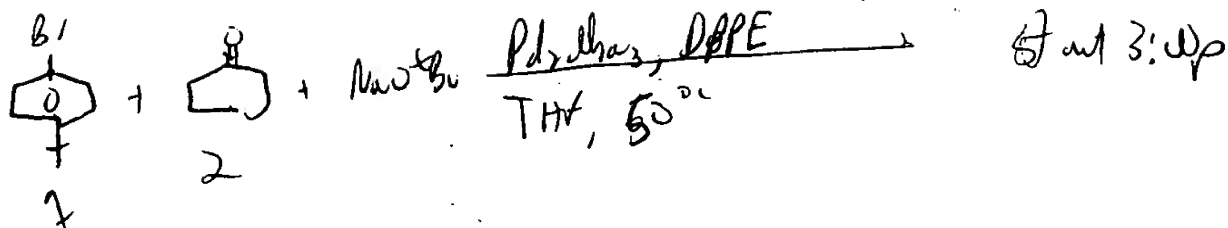
After 3 hrs, took aliquot - mp-6c-11-245-1 25% O=C1CCCC1 31% prod.  
 44% SM no O=C1CCCC1

12/1/91. 24 hrs, mp-6c-11-245-2 7.5% O=C1CCCC1  
 2% O=C1CCCC1  
 86% prod.

46.4443

46.3700

79.3 mg = 65% yield

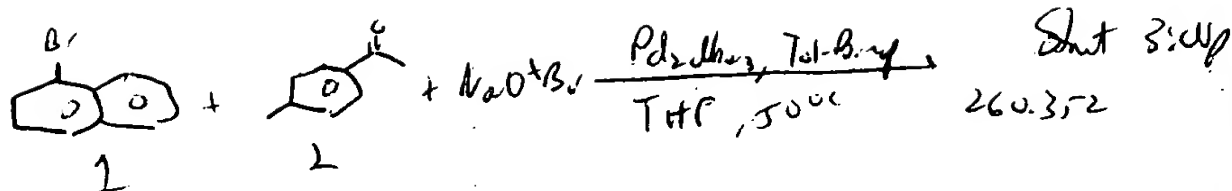


Compound	MW	equiv	mmole	amount	conc
1	213.12	1.0	2.5	90ul	
Cyclohexene	98.14	1.2	0.6	62ul	
NaO <sup>t</sup> Bu	96.7	1.3	0.65	65mg	
Pd <sub>2</sub> dbs <sub>3</sub>	915.2	0.015	0.005	6.4mg	
DPPE	<del>554.34</del> 402.47	0.031	0.010	<del>7.2mg</del> 7.2mg	
THF				3ml	

An oven dried Schlenk tube was charged w/ NaO<sup>t</sup>Bu, Pd<sub>2</sub>dbs<sub>3</sub>, DPPE and was evacuated and back filled w/ argon. To this was added 1, 2, THF and the resulting mixture heated to 50°C while under argon.

12/2 After 18 hrs - took aliquot MP 61-15-241-1 48 @<sup>+</sup>  
69g Sm  
no prod.

12/3/96 44hrs - took aliquot MP 61-10-246-2 78 @<sup>+</sup>  
62g Sm  
no prod



Compound	MW	equiv	mmole	amount	volume
1	202.08	1.0	0.5	108ul	
2	134.07	1.2	0.6	80ul	1.005
NaO <sup>+</sup> B <sup>-</sup>	96.7	1.2	0.65	65ms	
Pd <sub>2</sub> dhp <sub>2</sub>	915.7	0.015	0.0075	6.4u	
Tbl-B.ry	678.74	0.032	0.018	12.2mg	
THF				3ml	

12/21/91 - after = 18hrs, Took aliquot - MP-61-II-301-1 8% naphthalene  
 358 SM  
 44% - RT: 4.683

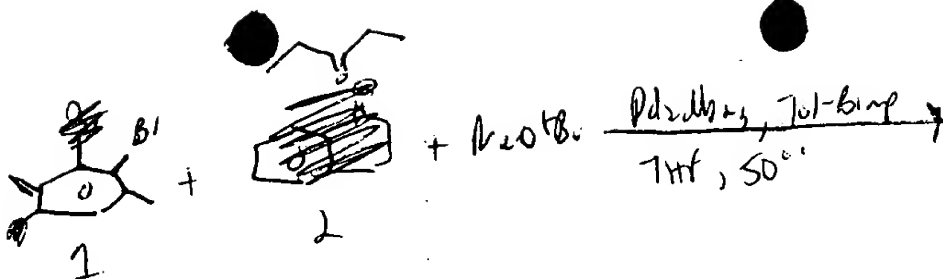
MP-61ms-II-301-1 MW=260

12/31/91 - after = 44 hrs, Took aliquot MP-61-D-301-2  
 4% reduced (naphthalene)  
 299 SM  
 59% prod RT: 9.246

43.5043

43.3480

106.3mg 82% yield



Start 3:00p

Compound	MW	gms	mmol	amount
1	185.07	1.0	0.50	67ul
2	<del>185.07</del> 86.17	1.2	0.60	64ul
NaOEt	96.7	1.3	0.65	65mg
Pd2dhs	915.7	0.025	0.025	6.4mg
Tol-Bing	678.79	0.032	0.018	12.2mg
THF				3ml

1.301

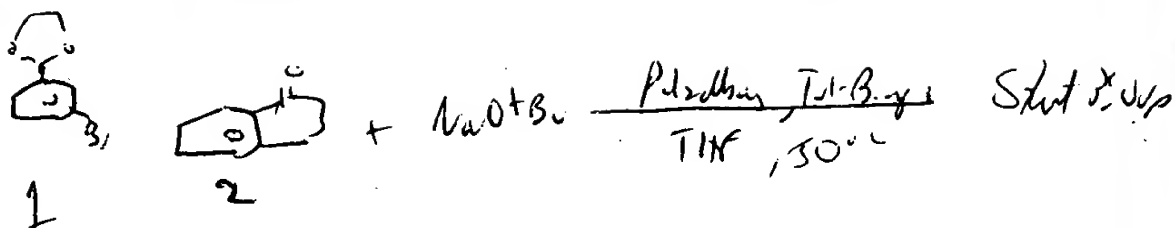
~~1.301~~ 0.812

12/2  
 After 18hrs - Took aliquot  
 MP-66-II-302-1 5% xylene  
 85% SM

12/3/96 After ~ 44 hours, Took aliquot  
 MP-66-II-302-2 4.6% xylene  
 82-89% SM

09/239,024

09/239,024



Compound	MW	mmole	equiv	amount	
1	229.03	1.0	0.5	76 ml	1.514
2	146.14	1.2	0.6	80 ml	
NaO <sup>+</sup> B <sup>-</sup>	96.7	1.3	0.65	65 mg	
Phthalic	95.7	0.015	0.0075	6.9 mg	
Tl-Bing	678.74	0.032	0.016	12.1 mg	
THF				3.2	

12/21/46 - after 18h, Task aliquot

MP 60-4-303-1

358 RT = 3.864

624 RT = 11.260

12/31/46 - after 44h Task aliquot

MP 60-4-303-2